13

CLAIMS

- 1. A waterproof vapor-permeable multilayer article, characterized in that it comprises at least one first layer (11, 111, 211, 311) made of a material that is vapor-permeable and microporous and is at least partially hygroscopic or can assume hygroscopic characteristics over time, and at least one second layer (12, 112, 212, 312) that is waterproof and vapor-permeable.
- 2. The multilayer article according to claim 1, characterized in that said at least one first layer (11, 111, 211, 311) comprises a base of polyolefin and filler particles.

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- 3. The multilayer article according to claim 2, characterized in that the molecular weight of said polyolefin is at least 500,000 g/mole.
- 4. The multilayer article according to claim 3, characterized in that the molecular weight of said polyolefin is preferably comprised between 4×10^6 g/mole and 7×10^6 g/mole.
- 5. The multilayer article according to one of claims 2 to 4, characterized in that said polyolefin is constituted by isotactic polypropylene or polyethylene.
- 6. The multilayer article according to one of claims 2 to 5, 20 characterized in that said filler is preferably silicon dioxide SiO₂.
 - 7. The multilayer article according to claim 6, characterized in that the average diameter of the filler particles of silicon dioxide SiO_2 are substantially comprised between 0.01 μm and 20 μm , while the average surface area of said fillers is substantially comprised between 30 m²/g and 950 m²/g.
 - 8. The multilayer article according to claim 6 or 7, characterized in that the average surface area of said filler particles is preferably at least $100 \text{ m}^2/\text{g}$.
- 9. The multilayer article according to one or more of the preceding claims, characterized in that said at least one first layer (11, 111, 211, 311)

14

made of microporous material has a pore size of less than 1 μm in diameter.

- 10. The multilayer article according to one or more of the preceding claims, characterized in that preferably more than 50% of the pores of said at least one first layer (11, 111, 211, 311) made of microporous material have a diameter of less than $0.5 \mu m$.
- 11. The multilayer article according to one or more of the preceding claims, characterized that the porosity of said at least one first layer (11, 111, 211, 311) made of microporous material is preferably at least 50%.
- 12. The multilayer article according to one or more of the preceding claims, characterized in that said at least one first layer (11, 111, 211, 311) made of microporous material has a thickness comprised between 200 μ m and 1.5 cm.

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- 13. The multilayer article according to claim 12, characterized in that said at least one first layer (11, 111, 211, 311) made of microporous material has a thickness comprised preferably between 200 μ m and 600 μ m.
- 14. The multilayer article according to claim 1, characterized in that said at least one first layer (11, 111, 211, 311) is constituted by a microporous membrane manufactured by the company DARAMIC Inc. and known commercially by the name DARAMIC®.
- 15. The multilayer article according to one or more of the preceding claims, characterized in that said at least one second waterproof vapor-permeable layer (12, 112) is constituted by a polypropylene-based microporous hydrophobic material.
- 16. The multilayer article according to claim 15, characterized in that the polypropylene of said microporous hydrophobic material is an isotactic homopolymer.
 - 17. The multilayer article according to claim 1 or 14, characterized in that said at least one second layer (12, 112) is constituted by a hydrophobic membrane manufactured by the company CELGARD Inc. and known commercially as CELGARD[®].

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- 18. The multilayer article according to claim 1, characterized in that said at least one second layer (12, 112) is composed of a polymer based on fluoropolymer or polysiloxane, said at least one second layer (12, 112) adhering to said first layer (11, 111) by spreading or immersing said first layer (11, 111) in a bath of said polymer.
- 19. The multilayer article according to claim 18, characterized in that said fluoropolymer is known commercially by the trade name Zonyl[®] and is manufactured by DuPont.
- 20. A method for manufacturing a multilayer article according to one of the preceding claims, consisting in:
 - preparing a solution or dispersion of the basic polymeric mix for said first layer (11, 111) in a volatile organic liquid with low surface tension, in order to produce a spreading solution that has a certain viscosity;
- applying said solution by spreading to the surface of said second layer (12, 112), which acts as a backing, in order to form a coating layer on its surface;
 - evaporating the volatile components of the spread in order to promote the cross-linking reaction of the spread surface;
 - drying the coating in order to remove the residual humidity.

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- 21. A method for producing a multilayer article according to one of claims 1 to 17, which consists in coupling said first layer (11, 111) and said second layer (12, 112) by lamination of one of said layers onto the other.
- 22. A method for producing a multilayer article according to one of claims 1 to 17, which consists in coupling said first layer (11, 111) in sheet form to said second layer (12, 112), also in sheet form, by applying adhesive spots or by using ultrasound or by means of high-frequency welding.
- 23. The multilayer article according to one or more of claims 1 to 14, characterized in that said at least one second layer (212, 312) is constituted by a film obtained by means of a plasma deposition treatment.

16

- 24. The multilayer article according to claim 23, characterized in that said plasma deposition treatment is obtained by working in high-vacuum cold plasma conditions.
- 25. The multilayer article according to claim 23 or 24, characterized in that said plasma deposition treatment is obtained by using a radiofrequency generator so that the electrical field in the treatment oscillates with a frequency substantially comprised between 13 MHz and 14 MHz.
- 26. The multilayer article according to claim 25, characterized in that said plasma deposition treatment is obtained by using a radiofrequency generator so that the electrical field in the treatment oscillates with a frequency preferably on the order of 13.56 MHz.

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- 27. The multilayer article according to one of claims 23 to 26, characterized in that said plasma deposition treatment is obtained by using a power of the electrical field applied in the treatment that is substantially comprised between 50 watts and 700 watts.
- 28. The multilayer article according to one of claims 23 to 27, characterized in that the duration of said plasma deposition treatment for a siloxane-based monomer is comprised between 160 and 600 seconds.
- 29. The multilayer article according to claim 28, characterized in that the duration of said plasma deposition treatment for a siloxane-based monomer is substantially equal to 420 seconds.
 - 30. The multilayer article according to one of claims 23 to 29, characterized in that the level of vacuum in said plasma deposition treatment is substantially comprised between 10⁻¹ mbar and 10⁻⁵ mbar.
 - 31. The multilayer article according to claim 23, characterized in that said plasma deposition treatment is obtained by working in high-vacuum cold plasma conditions and by using a radiofrequency generator so that the electrical field in the treatment oscillates with a frequency on the order of 13.75 MHz, with an applied electrical field power of 300-500 watts, and a

17

vacuum level comprised between 10⁻¹ and 10⁻⁵ mbar.

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- 32. The multilayer article according to one of claims 23 to 31, characterized in that the plasma deposition precursor material is a siloxane-based monomer.
- 33. The multilayer article according to one of claims 23 to 31, characterized in that the plasma deposition precursor material is an oil-repellent and water-repellent fluoropolymer.
- 34. The multilayer article according to one of claims 23 to 31, characterized in that the material of said at least one second layer (212, 312) is a polysiloxane.
 - 35. The multilayer article according to one of claims 23 to 31, characterized in that the material of said at least one second layer (212, 312) is an oil-repellent and water-repellent fluoropolymer.
- 36. The multilayer article according to claim 33 or 35, characterized in that said fluoropolymer is known commercially by the trade name Zonyl® manufactured by DuPont.
 - 37. A method for producing a multilayer article according to one of the preceding claims 23 to 34, comprising the steps of:
 - loading said first layer (211, 311) to be coated into the reaction chamber,
 - bringing said reaction chamber to a preset vacuum pressure;
 - starting plasma generating electrical discharge;
 - injecting the vaporized precursor monomer into said reaction chamber;
- 25 waiting for a preset deposition time.
 - 38. A production method according to claim 37, characterized in that it comprises a pretreatment step that consists in the surface cleaning of said first layer (211, 311) by subjecting it to an inert gas that is injected into said reaction chamber.